The Effect of Various Hardeners on the Mechanical and Thermal Properties of Epoxy Resin

Najuma Abdul Razack, Lity Alen Varghese

Department of Chemical Engineering, National Institute of Technology, Calicut, Kerala,India.

Abstract

Epoxy resins have been known to possess good mechanical properties and excellent adhesive properties and thus have been widely used in industry, such as adhesive, coating, laminating and composite applications. In this study , a low molecular weight epoxy resin, diglycidyl ether of bisphenol A (DGEBA) is cured with both aliphatic and aromatic hardeners and a comparison was done based onmechanical characterization, Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) studies. Four different hardeners (2 aliphatic and 2 aromatic) were used in the stoichiometric amounts for the study. They include Triethylene tetramine (TETA), Dicyandiamide (DICY), Diaminodiphenyl sulphone (DDS), and m-phenylenediamine (mPDA). The mechanical characterization comprised the shear and peel strength experimentations which concluded that the aromatic ones are better compared to the aliphatic ones. From the DSC studies the effectiveness was found to be in the order TETA<DICY<DDS<mPDA which was consistent with the thermo gravimetric analysis (TGA) studies.
Keywords* — *curing, epoxy resin, hardener, mechanical properties, thermogravimetric analysis.

1. Introduction

Epoxy resins forms a big class of compounds containing two or more epoxy groups, which reacts with a variety of curing agents containing active hydrogens such as amines and anhydrides[1]. These resins linked with amine hardeners are widely used as structural adhesives because they have good thermal and mechanical properties [2]. Amine compounds are classified into primary, secondary, and tertiary amines, in which one, two, and three hydrogen molecule(s) of ammonia (NH_3) have been substituted for hydrocarbon, respectively. Amines are called monoamine, diamine, tri-amine, or polyamine according to the number of amines in one molecule. According to the types of hydrocarbons involved, amines are classified into aliphatic, alicyclic and aromatic amines and they all are important curing agents for epoxy resin. Resins that have been cured using aliphatic amines are strong, and are excellent in bonding properties. They have resistance to alkalis and some inorganic acids, and have good resistance to water and solvents, but they are not so good to many organic solvents. Aromatic amine has been developed to achieve greater heat resistance and chemical resistance than those of aliphatic amine.

Depending on the crosslinking agent, the final properties of the epoxy network are also different. It was observed that the properties and performance of cured compounds of epoxy resins are dependent on the type of curing agent and curing conditions [3]. When the curing agent is an aliphatic amine, the curing process occurs at room temperature, but the reaction is slow [4]. On the other hand epoxy resins cured with aromatic amines generally present good thermal and chemical resistance.Sometimes the aromatic ring was introduced into epoxy backbone during synthesis, for example, naphthalene ring and biphenyl group were often used to improve the heat resistance of epoxy resin [5-9].

During cure of aliphatic amines, each primary aliphatic amine reacts with an epoxy group of DGEBA, via ring opening, to form a CH_2-NH bond and a pendant hydroxyl group, the presence of which is known to accelerate subsequent ring opening reactions. The resulting secondary amines react in a similar manner with remaining epoxy rings to crosslink the polymer chains, though at a slower rate.

In the aromatic amines, the amine group is separated by rigid benzene rings rather than flexible chains of molecules as in the aliphatic amines [10]. The stoichiometric relationship between curing agents and resins has a great effect on the physical and the mechanical properties of the epoxy resin.

Four different amines were chosen for the present study, viz. Triethylene tetramine, Dicyandiamide, Diaminodiphenyl sulphone and m-phenylenediamine. The amine/epoxy reaction occurs at room temperature and it can be accelerated with an elevated temperature cure [11]. TETA is a common primary polyamine which is in the liquid form, having a pot life of 30 min at 75^0F. DICY is the most commonly employed latent curing agent that forms crystals having a high melting point of 207°C to 210°C. It is the dimer of cyanamide and is amphoteric. However cyclisations take place easily and the nitrile group is less reactive.DICY has a pot life of 24 hours when it is dissolved in epoxy resin using a solvent or the like, but it is normally used in the form of fine powder dispersed in the resin, which has a very long pot life of 6 to 12 months. Such compositions are stable at room temperature but cures at high temperatures of 160°C to 180°C in 20 to 60 minutes, and generates a large quantity of heat during curing[12]. Thus, it has used only in thin films such as paints, adhesives, and laminates.

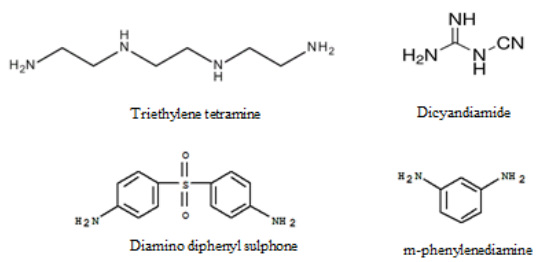

Figure 1: Chemical structures of the various curing agents used.

Aromatic amines are generally solid curing agents, DDS and m-PDA being the typical ones. DDS is commonly employed in aerospace laminating applications requiring enhanced honey-comb peel strength [13]. mPDA, being tetrafunctional, each molecule reacts with four units of resin to form a tridimensional network [14]. This system is widely used as an adhesive because it is easy to make and has good resistance to aging in an aggressive chemical medium. In addition to the adhesive properties like lap shear strength and Peel strength of the epoxy formulations, the thermal properties and DSC studies of the various systems are also presented in this paper.

2. Materials and Methods

The epoxy resin (Epofine-1556, diglycidyl ether of bisphenol-A with epoxide equivalent weight 5.2 eq/Kg) was obtained from Fine Finish Organics Pvt. Ltd, Mumbai. The curing agents DICY, TETA, DDS and mPDA were obtained from Sigma Aldrich. The epoxy resin was mixed with hardeners in the stoichiometric ratios and was cured at the specified temperatures for 1 hour.

3. Measurements

3.1 Mechanical properties

The mechanical properties are often the most important properties related for technology. This is because virtually all service conditions involve some degree of mechanical loadings.

Aluminium strips of size 100x25 mm were machined from 0.8 mm thick sheets to serve as metal substrates for peel studies on metal-to-metal bonds. Strips of 100x25x1 mm were used for shear strength. Surface preparation is necessary before the application of adhesive. Solvent degreasing was done with trichloroethylene, to remove dust and traces of oily impurities on the surface. Following the solvent wiping, the surface was abraded with emery paper (P 100) and is again wiped with solvent to remove completely the debris of abrasion. An even contact pressure is applied throughout the joining surface after the application of the adhesive and it is then kept in the oven at the required temperature for the specified time.

Peel strength and lap shear strength of metal-to-metal specimens were determined on a universal testing machine as per ASTM D 903[15] and ASTM D 1002[16] respectively with a grip separation rate of 50 mm/min at room temperature.

3.2 Thermogravimetric analysis

Thermogravimetric analysis (TGA) is an analytical technique used to determine a material'sthermal stability and its fraction of volatile components by monitoring the weight change thatoccurs as a specimen is heated. The measurement is normally carried out in air or in an inertatmosphere, such as Helium or Argon, and the weight is recorded as a function of increasingtemperature.

Thermogravimetric analysis involves heating a sample in an inert or oxidising atmosphere and measuring the weight. The weight change over specific temperature ranges provides indications of the composition of the sample and thermal stability. In the present study, the samples (3-5 mg) were heated from room temperature to 750^{0}C at a heating rate of 10^{0}C/min under nitrogen atmosphere.

3.3 Differential Scanning Calorimetry

The basic principle underlying this technique is that when the sample undergoes a physical transformation such as phase transitions, more or less heat needs to flow to it than the reference to maintain both at the same temperature. Whether less or more heat must flow to the sample depends on whether the process is exothermic or endothermic.

DSC can investigate various characteristics of epoxy systems, including glass transition temperatures before and after curing, as well as the temperature and reaction calories during the curing reaction. All samples (3-5 mg) were prepared in sealed aluminium pans and the non-isothermal scans were performed under nitrogen atmosphere at 10^0C/min over a temperature range of 0-300^0C.

4. Results and Discussion

4.1 Mechanical characterization

Mechanical characterization mainly comprises of the lap shear and peel strength. Lap shear determines the shear strength of adhesives for bonding materials when tested on a single-lap-joint specimen.The test is applicable for determining adhesive strengths, surface preparation parameters and adhesive environmental durability. Peel strength is the average load per unit width of bond line required to part bonded materials.Peel tests involve stripping away a flexible adherend from another adherend that may be flexible or rigid. The average lap shear and peel strengths of the various formulations are given in table 1. From the results, it is clear that aromatic amines gave better strength characteristics compared to the aliphatic amines.

Table 1. Average lap shear and peel strength values for various curing agents.

Curing Agent	Average lap shear strengths (N/mm^2)	Average Peel strength (N/mm)
Triethylene tetramine (TETA)	0.384	0.272
Dicyandiamide (DICY)	0.547	0.333
Diamino diphenylsulphone (DDS)	0.614	0.706
m-Phenylene diamine (mPDA)	0.952	1.240

4.2 Thermogravimetric analysis

Thermogravimetric analysis is mainly used in the assessment of thermal stability and decomposition temperature. The two most important pieces of information from TGA is the weight loss onset temperature (T_{onset}) and the residual mass (M_{res}). The weight loss onset temperature is the temperature at which the oxidation just begins. So if T_{onset} is more, it indicates that the sample is more stable and that it can be used for high temperature applications.

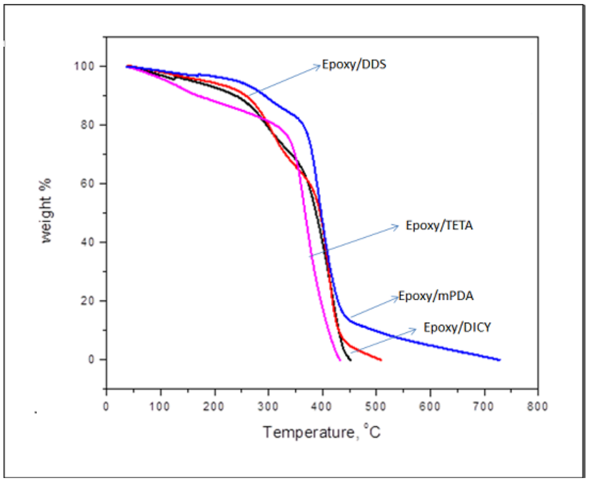

Figure2: Thermogravimetric Analysis curves for various epoxy/hardener systems.

A comparison of the TGA curves for the various systems are given in Figure 2, from which it is clearly understood that there was no loss of material upto around 250^0C, which signifies the system can be used for elevated temperature applications. Eventhough aromatic amines have less electron density on nitrogen than aliphatic amines, the resin cured with aromatic amine shows higher thermal and chemical resistance property due to the presence of rigid and thermally stable aromatic rings apart from the fact that they are less reactive.

4.3 Differential Scanning Calorimetry

DSC provides information regarding the curing reaction heat and glass transition temperature, T_g of thermosetting resins.

Table 2. DSC analysis data for various systems

Sample	Glass Transition	
	Onset Temperature (^OC)	Peak Temperature (^OC)
Epoxy / TETA	93.85	96.84
Epoxy / DICY	94.61	95.64
Epoxy / DDS	74.53	76.26
Epoxy / mPDA	46.83	48.54

Table 2 provides the glass transition onset temperatures and peak temperatures for the various systems. As the peak temperature increases, the reaction becomes less effective. From the results, it is clear that, the aliphatic amines are having higher peak temperatures, when compared to aromatic amines.

Aromatic amines are less basic than aliphatic amines, mostlybecause of resonance. But aromatic amine ismore stabilized compared to its ammonium ion than analiphatic amine is compared to its ammonium ion.

5. Conclusion

Epoxy adhesives are almost unmatched in heat and chemical resistance among common adhesives. In the present study, an effort has been done to find out the effect of various hardeners on the epoxy resin. The study was also meant to compare the behavior of aliphatic and aromatic amines. From the mechanical characterization and DSC studies, it can be concluded that the effectiveness of the system varies in the order mPDA > DDS > DICY > TETA. Variation in thermal stability was also found to follow the same order. Hence we concluded that aromatic amines are better compared to aliphatic amines.

Acknowledgement

The authors would like to acknowledge Sophisticated Analytical Instrumentation Facility (SAIF), STIC, Cochin University of Science and Technology, India for the help rendered with TGA and DSC analysis.

6. References

[1] Chaofu Wu and Weijian Xu, "Atomistic molecular modeling of crosslinked epoxy resin", Polymer,47, pp. 6004–6009 (2006).
[2] V. Nassiet, J.P. Habas, B. Hassoune-Rhabbour, Y.Baziard and J.A.Petit., "Correlation between viscoelastic behavior and cooling stresses in a cured epoxy resin system",Journal Of Applied Polymer Science, 99, pp. 679–690 (2006).
[3] R. Jain, P. Kukreja, A. K. Narula and V. K. Chaudhary, "Studies of the curing kinetics and thermal stability of epoxy resins using a mixture of amines and anhydrides", Journal of Applied Polymer Science, 100, 3919 (2006).
[4] S.G. Prolongo, Gilberto del Rosario, and A.Urena, "Comparative study on the adhesive properties of different epoxy resins", International Journal of Adhesion and Adhesives, 26, 125(2006).
[5] Chun-Shan Wang and Ming-Chun Lee, "Synthesis and modification of a naphthalene containing trifunctional epoxy resin for electronic applications", Journal of Applied Polymer Science, 70, 1907 (1998).
[6] Chun-Shan Wang and Ming-Chun Lee, "Synthesis, Characterization and properties of multifunctional naphthalene containing epoxy resins cured withcyanate ester",Journal of Applied Polymer Science, 73, 1611(1999).
[7] M. Kaji and T. Endo, "Synthesis of a novel epoxy resin containing naphthalene moiety and properties of its cured polymer with phenol novolac", Journal of Polymer Science Part A:Polymer Chemistry, 37, 3063 (1999).
[8] Z-Q. Cai, J. Sun, Q. Zhou and J. Xu, "Synthesis and characterization of a novel liquid-crystalline epoxy resin combining biphenyl and aromatic ester-type mesogenic units", Journal of Polymer Science Part A:Polymer Chemistry, 45, 727 (2007).
[9] S. Han, H. G. Yoon, K. S. Suh, W. G. Kim and T.J. Moon, "Cure kinetics of biphenyl epoxy-phenol novolac resin system using triphenylphosphine as catalyst", Journal of Polymer Science Part A:Polymer Chemistry, 37, 713 (1999).
[10] Najat.J.Saleh, Adnan.A.AbdulRazack, Manal.A.Tooma, and Mariam. E.Aziz, "A study on mechanical properties of epoxy resin cured at constant curing time and temperature with different hardeners", Engg. & Tech. Journal, 29, pp. 1804–1818 (2011).
[11] E.M.Petrie, Handbook of Adhesives And Sealants, McGraw- Hill, New York , 361 (2000).
[12] ManilalSavla, Epoxy Resin Adhesives, in Handbook of Adhesives, Skiest, I., 3rd ed., pp.440,Van Nostrand Reinhold Company, Newyork (1977).
[13] C.Gouri, R.Ramaswamy and K.M.Ninan, "Studies on the adhesive properties of solid elastomer-modified novolac epoxy resin", Int. Journal Of Adhesion and Adhesive, 20, pp. 305–314 (2000).
[14] V. Nassiet, J.P. Habas, B. Hassoune-Rhabbour, Y.Baziard and J.A.Petit., "Correlation between viscoelastic behavior and cooling stresses in a cured epoxy resin system", Journal Of Applied Polymer Science., 99, pp. 679–690 (2006).
[15] ASTM D903 standard.
[16] ASTM D1002 standard.